Journal of the Korean Physical Society, Vol. 56, No. 2, Fabruary 2010, pp. 576∼579

Electrical Resistivity and Transmittance Properties of Al- and Ga-codoped ZnO Thin Films

Jungwoo KANG, Hyoun Woo KIM and Chongmu LEE*

Department of Materials Science and Engineering, Inha University, Incheon 402-751

(Received 11 August 2009, in final form 12 October 2009)

Films were deposited on glass substrates by sputtering gallium-doped zinc oxide (GZO) (Ga_2O_3: 90 wt%, ZnO: 10 wt%) and aluminum-doped zinc oxide (AZO) (Al_2O_3: 3 wt%, ZnO: 97 wt%) targets simultaneously using a direct-current (DC)/radio-frequency (RF) magnetron cosputtering system. The concentration of gallium (Ga) in the film was varied by using different RF powers for sputtering the GZO target with the DC power for sputtering the AZO target fixed. A minimum resistivitywas obtained at an RF sputtering power of 200 W for the GZO target when the DC sputtering power for the AZO target was fixed at 60 W. It was found that the resistivity of AZO thin films (6.40×10^{-3} Ω-cm for 0 W) could be lowered by more than one order by cosputtering AZO and GZO targets to make AGZO thin films (2.14×10^{-3}Ω-cm for 200 W) without lowering their transmittance at all. In addition, the origin of the enhancement in the electrical property of the AZO by additional Ga doping is discussed.

PACS numbers: 73.61.Ga, 78.68.+m, 81.15.-z
Keywords: AlGaZnO (AGZO), Transparent conducting oxide (TCO), Cosputtering, Transmittance, Electrical resistivity
DOI: 10.3938/jkps.56.576

I. INTRODUCTION

It is essential to use transparent conducting oxides (TCOs) in optoelectronic devices such as solar cells and flat panel displays. Indium tin oxide (ITO) has been most widely used as a TCO for these applications because it has a low electrical resistivity, a high visible transmittance, and a relatively high work function [1]. However, the cost of preparing ITO films is very expensive because indium is a rare and expensive element. Hence, to date various TCO materials, such as F-doped SnO_2, Sb-doped SnO_2, Al-doped ZnO (AZO), and Ga-doped ZnO (GZO), have been developed as alternatives to ITO and are used these days [2–9]. Impurity-doped ZnO has several advantages over ITO although the resistivity of ZnO is somewhat higher than that of ITO. These advantages include lower cost, higher etchability, higher resistance to hydrogen plasma reduction, and lower synthesis temperature. In particular, impurity-doped ZnO is more favorable than ITO for amorphous silicon solar cells fabricated on transparent conducting (TC) substrates, because the TC substrates are exposed to a hydrogen plasma [10,11]. The lowest resistivity of AZO thin films obtained to now is reported to be lower than that of GZO thin films. However, Ga has several advantages over Al as an n-type impurity in ZnO:

(1) Al is easily oxidized during deposition whereas Ga is more resistant to oxidation [12].

(2) The ZnO lattice distortion is minimal even for a high concentration of Ga in ZnO because the Ga-O bond length (0.192 nm) is close to the Zn-O bond length (0.197 nm). Consequently, fewer defects are generated in GZO than in AZO [13].

(3) Ga causes maller diffusion-related problem because the diffusivity of Ga is lower than that of Al.

AZO and GZO have merits and demerits over each other, as discussed above. Therefore, it is necessary to check if the electrical and the optical properties of AGZO are better than those of AZO and GZO. There have been numerous reports on AZO and GZO thin films, but almost no reports on AGZO thin films yet. In this paper, we report the electrical properties and the transmittance properties of AGZO thin films.

II. EXPERIMENTS

Ga, Al-doped ZnO (GAZO) films were deposited on Corning 1737 glass substrates by sputtering 2-inch GZO (Ga_2O_3: 90 wt%, ZnO: 10 wt%) and 2-inch AZO (Al_2O_3: 3 wt%, ZnO: 97 wt%) targets simultaneously by using a DC/RF magnetron cosputtering system. The glass surfaces were cleaned in an ultrasonic cleaner for 10 min

*Corresponding Author; E-mail: cmlee@inha.ac.kr;
Tel: +82-32-860-7536; Fax: +82-32-873-7537

Table 1. Sputtering powers and times for each AGZO thin film.

Sample No.	Sputtering power(W) GZO target	Sputtering power(W) AZO target	Sputtering time (min)
A	RF[a]0	DC[b]60	25
B	RF 100	DC 60	15
C	RF 200	DC 60	10
D	RF 300	DC 60	5

[a]RF-power was applied to the GZO target.
[b]DC-power was applied to the AZO target.

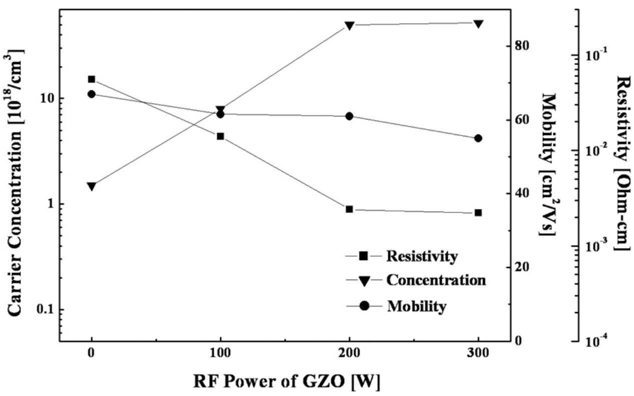

Fig. 1. Dependence of the carrier concentration, carrier mobility, and resistivity of AGZO thin films on the RF power for sputtering the GZO target. The DC power for sputtering the AZO target was fixed at 60 W.

with acetone and methanol and were then blown dry with nitrogen before they were introduced into the magnetron sputtering system. The deposition chamber was initially evacuated to 5.5×10^{-5} Torr, and argon (Ar) gas was introduced into the chamber to maintain the desired pressure (1.2×10^{-2} Torr). The substrate temperature and the Ar gas flow ratio were room temperature and 30 sccm, respectively. The radio-frequency (RF) sputtering power for the target was varied to make four kinds of GAZO thin film samples with different compositions as shown in Table 1. The sputtering times were controlled to obtain film thicknesses in the range of 170 - 200 nm.

For these four different kinds of samples, X-ray diffraction (XRD) analyses were performed (RIGAKU 2500PC) to investigate the crystallinity of the AGZO films. The full-width-at-half-maximum (FWHM) values were measured from the ZnO (002) intensity peaks of the XRD patterns to assess the crystallinity of the AGZO films. The X-ray reflectivity (XRR) technique (X PET-PRO MRD) was used to measure the thicknesses of the TCO films. The carrier concentrations, carrier mobilities, and electrical resistivities of the films were determined by using Hall effect measurement (HEM-2000). The optical transmittances were measured by using a spectrophotometer (CARY SE, VARIAN).

III. RESULTS AND DISCUSSION

The carrier concentrations, carrier mobilities, and electrical resistivities of the GAZO thin films are plotted as a function of the RF sputtering power for the GZO target in Fig. 1. The figure shows that the resistivity of the GZO thin films is decreased by a certain level of Ga doping, but further Ga doping does not influence the resistivity. In other words, a minimum resistivity is obtained at an RF sputtering power of 200 W for the GZO target with the DC sputtering power for the AZO target fixed at 60 W. This result suggests that the resistivity of the AZO thin films ($6.40 \times 10^{-3}\Omega$-cm for 0 W) can be lowered by more than one order by cosputtering AZO and GZO targets to make AGZO thin films ($2.14 \times 10^{-3}\Omega$-cm for 200 W). The lowest resistivity of the AGZO thin films obtained in this work is about one order higher than the lowest one obtained for the impurity-doped ZnO thin films reported to date [14–16]. We did not optimize the process parameters, including the oxygen partial pressure, to minimize the resistivity because the main issue in this work was to investigate the additional doping effect in AGZO thin films. There have been many reports that the resistivity varies a lot depending on the film deposition method and the deposition process parameters [17]. The carrier concentration tends to increase, but the carrier mobility tends to decrease as the RF power for GZO increases. However, those changes are not linear. In particular, the carrier concentration increases quite a bit as the RF power is increased from 0 to 200 W, but it increases a little bit as the RF power is increased from 200 to 300 W. The lower rate of increase of the carrier concentration in the power range of 200-300 W may be explained as follows:

As the RF power is increased further than 200 W, the sputtering rate slightly decreases because the sputter deposition rate is known to change parabolically with the sputtering power. A larger portion of the Al dopant atoms fail to occupy substitutional sites, but stay at interstitial sites in heavily-doped ZnO, which results in carrier trapping.

On the other hand, the highest velocity of electrons in a material is $\sim 10^7$ cm/sec. The actual speed of electrons is much lower than this because the mobility of the electrons in a material is decreased by various scattering processes. In semiconductors and semimetals, there are several possible scattering mechanisms for electrons: phonon scattering, ionized impurity atom scattering, neutral impurity atom scattering, electron-electron and electron-hole scattering, crystal defect scattering, and surface roughness scattering. Phonon scattering is important at high temperatures whereas ionized impurity atom scattering, electron-electron scattering, and electron-hole scattering are important at high dopant

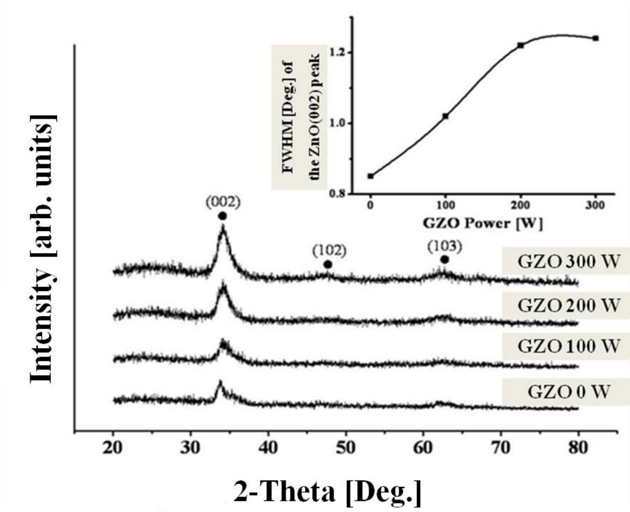

Fig. 2. X-ray diffraction patterns and FWHM of the ZnO (002) peak (inset) of AGZO thin films deposited by sputtering AZO and GZO targets simultaneously at different RF powers for GZO at a DC power of 60 W for AZO.

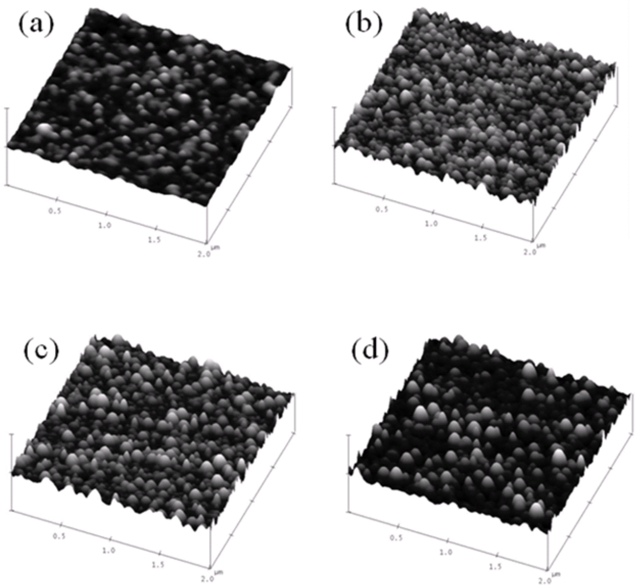

Fig. 3. AFM images of the surfaces of AGZO thin films deposited by sputtering AZO and GZO targets simultaneously at different RF powers for GZO and a DC power of 60 W for AZO.

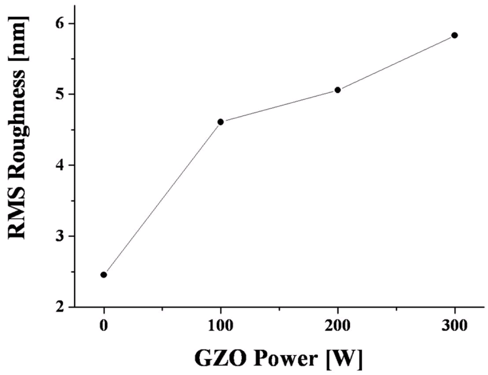

Fig. 4. RMS surface roughness of the AGZO thin film as a function of the RF power for sputtering the AZO target.

concentrations. Neutral impurity scattering is usually negligible. The carrier mobility tends to decrease as the RF power for GZO is increased (Fig. 1). This may be attributed to ionized impurity atom scattering. As the power is increased, the total carrier concentration increases, and, in turn, the ionized impurity atom scattering increases. If the temperature at which a transparent conducting oxide (TCO) material is actually used is fixed at room temperature and if the dopant concentration in the TCO is also fixed by fixing the power at a constant value, crystal defect scattering and surface roughness scattering are the two scattering mechanisms important in our TCO system. These two scattering mechanisms strongly depend on the deposition process parameters for the TCO thin films as follows:

For crystal defect scattering due to the crystallographic defects in the lattice, Fig. 2 shows the XRD patterns of AGZO films deposited at different RF powers for GZO. The FWHM of the ZnO (002) peak measured from the XRD data is plotted as a function of the GZO power in the inset of Fig. 2. The FWHM tends to increase, in other words, the crystallinity of the ZnO films is degraded as the RF power increases. This result suggests that the ZnO lattice becomes more severely distorted and has a higher density of defects, such as dislocations, as the Ga doping concentration increases, although the radius of Ga^{3+} (0.062 nm) is closer to that of Zn^{2+} (0.060 nm) than that of Al^{3+} (0.053 nm). For Surface roughness scattering is a short-range scattering process arising from interface disorder and limits the mobility of two-dimensional electrons at the interface of the TCO layer and an adjacent layer. There are numerous reports on surface roughness scattering of electrons in semiconductors and semimetals. A good report on the quantum mechanical mobility model for scaled MOS transistors with emphasis on the surface roughness scattering is given in Ref. 18 of this paper as an example. Surface roughness scattering is well known to be particularly important in MOS devices because charge carriers move in a direction parallel to the Si-SiO_2 interface in the devices. Figure 3 shows the AFM images of the surface of the AGZO films deposited at different RF powers for GZO and a constant DC power of 60 W for AZO. The root-mean-square (RMS) surface roughness values of the AGZO films are also presented as a function of the DC power for GZO in Fig. 4. The surface of the AGZO films tends to become rougher as the DC power increases. Heavier doping seems to result in not only a lattice distortion but also a surface roughening of the AGZO thin films. A rougher surface certainly leads to

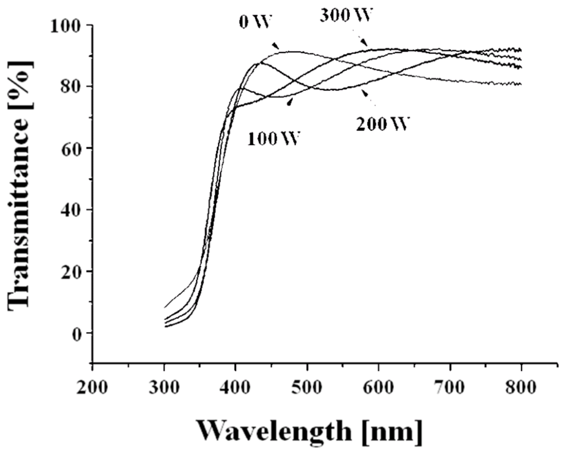

Fig. 5. Optical transmittance spectra for AGZO thin films deposited by cosputtering at different RF powers for GZO and a DC power of 60 W for AZO.

a more severe surface scattering, and that surface scattering, in turn, leads to a further decrease in the carrier mobility.

As discussed above, the carrier concentration increases, but the carrier mobility decreases as the sputtering power for GZO increases (Fig. 1). Therefore, the lowest resistivity seems to be obtained at 200 W, where the carrier concentration and the carrier mobility are traded off.

On the other hand, the optical transmittance spectra of the AGZO films for different sputtering powers for GZO are displayed in Fig. 5. The figure indicates that the transmittance of AGZO thin films is nearly the same as that of the AZO thin films (for 0 W), regardless of the concentrations of Al and Ga in the AGZO thin films. All the transmittance values for the four transmittance curves are almost in the same range, *i.e.*, from ∼77 to 90% in the visible wavelength range from 400 to 800 nm.

IV. CONCLUSION

In this work, AGZO films were deposited on glass substrates by sputtering GZO and AZO targets simultaneously using a DC/RF magnetron cosputtering system. The concentration of Ga in the film was varied by using different RF powers for sputtering the GZO target with the DC power for sputtering the AZO target fixed. Our results show that the resistivity of the AZO thin films ($6.40 \times 10^{-3}\Omega$-cm for 0 W) can be lowered by more than one order by cosputtering AZO and GZO targets to make AGZO thin films ($2.14 \times 10^{-3}\Omega$-cm for 200 W) without lowering their transmittance at all. The optimum RF sputtering power of the GZO target for the lowest resistivity when the DC sputtering power for the AZO target is fixed at 60 W is 200 W for which the carrier concentration and the carrier mobility are traded off.

ACKNOWLEDGMENTS

This work was supported by Inha University.

REFERENCES

[1] H. L. Hetnagel, A. L. Dawar, A. K. Jain and C. Jagadishi, *Superconducting Transparent thin Films* (Institute of Physics Publishing, Bristol and Philadelphia, 1995).
[2] M. Hiramatsu, K. Imaeda, N. Horino and T. Goto, J. Vac. Sci. Technol. A **16**, 669 (1998).
[3] M. Chen, Z. L. Pei, C. Sun, J. Gong, R. F. Huang and L. S. Wen, Mater. Sci. Eng. B **85**, 212 (2001).
[4] K. Yim, H. Kim and C. Lee, J. Electroceram. **17**, 875 (2006).
[5] K. Yim and C. Lee, J. Mater. Sci.: Mater. Electron. **18**, 385 (2007).
[6] S. Kim, W. Lee and C. Lee, Mater. Sci. Technol. **23**, 303 (2007).
[7] C. Lee, S. Kim, H. Kim and W. Lee, J. Kor. Phys. Soc. **50**, 586 (2007).
[8] W. Lee, R. P. Dwivedi, C. Hong, H. W. Kim and C. Lee, J. Mater. Sci. **43**, 1159 (2008).
[9] C. Lee, A. Park, Y. Cho, M. Park, W. I. Lee and H. W. Kim, Ceram. Int. **34**, 1093 (2008).
[10] S. Mayer and K. L. Chopra, Sol. Energ. Mater. **17**, 319 (1998).
[11] H. A. Wanka, E. Lotter and M. B. Schbert, Mater. Res. Soc. Symp. Proc. **336**, 657 (1994).
[12] H. J. Ko, Y. F. Chen, S. K. Hong, H. Wenisch and T. Yao, D. C. Look, Appl. Phys. Lett. **77**, 3761 (2000).
[13] V. Assuncao, E. Fortunato, A. Marquesa, H. Aguasa, I. Ferreira, M. E. V. Costa and R. Martins, Thin Solid Films **427**, 401 (2003).
[14] T. Minami, H. Nanto and S. Takata, Japan. J. Appl. Phys. **23**, L280 (1984).
[15] T. Minami, H. Sato, H. Nanto and S. Takata, Japan. J. Appl. Phys. **25**, L280 (1986).
[16] T. Minami, T. Miyata and T. Yamamoto, J. Vac . Sci. Technol. A **17**, 1822 (1999).
[17] See, for example, T. Minami, Semicond. Sci. Technol. **20**, S 35 (2005) and references therein.
[18] Y. Zhang and M. H. White, Solid State Electron **52**, 1810 (2008).